



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) Publication number:

0 554 968 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 93250038.2

(51) Int. Cl. 5: C10G 11/18, C10G 11/02,
B01J 21/00, B01J 29/00

(22) Date of filing: 01.02.93

(30) Priority: 05.02.92 US 831610
09.10.92 US 959023

(71) Applicant: W.R. Grace & Co.-Conn.
Grace Plaza, 1114 Avenue of the Americas
New York, New York 10036-7794(US)

(43) Date of publication of application:
11.08.93 Bulletin 93/32

(72) Inventor: Kim, Gwan
18917 Clover Hill Lane
Olney, MD 20832(US)

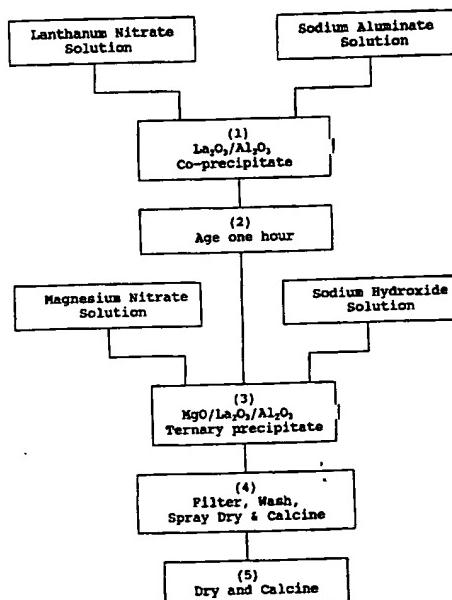
(84) Designated Contracting States:
DE ES FR GB IT NL

(74) Representative: UEXKÜLL & STOLBERG
Patentanwälte
Beselerstrasse 4
W-2000 Hamburg 52 (DE)

(54) Metal passivation/SOx control compositions for FCC.

(57) A composition comprising a coprecipitated magnesia-lanthana-alumina ($MgO-La_2O_3-Al_2O_3$) wherein the MgO component is present as microcrystalline phase, having a BET (N_2) surface area of at least 130 m^2/g , preferably part of which contains a catalytic oxidation and/or reducing promoter metal such as ceria, vanadia and/or titania, is combined with an FCC catalyst which is used to catalytically crack a hydrocarbon feedstock that contains metal and/or sulfur.

FIGURE 1



This application is a continuation-in-part of my U.S. Serial No. 831,610, filed February 5, 1992.

The present invention relates to compositions which are used to control SO_x emission and the adverse effects of metals such as V and/or Ni encountered in fluid catalytic cracking (FCC) operations, and more particularly to compositions that passivate Ni and/or V during the catalytic cracking of hydrocarbons as well as control SO_x emissions during oxidation regeneration of the catalysts.

5 Compositions which have been used to passivate Ni and/or V as well as control SO_x emissions typically comprise magnesia, alumina and rare earth oxides.

In particular, U.S. 4,472,267, U.S. 4,495,304 and U.S. 4,495,305 disclose compositions which contain magnesia-alumina spinel supports in combination with rare-earths such as ceria and lanthana, and U.S. 10 4,836,993 discloses the preparation of magnesium aluminate ($MgAl_2O_4$) and magnesia-alumina composites that are combined with a rare earth and used as sulfur oxide absorbent in FCC processes.

While prior compositions have been successfully used to control the adverse effects of V and/or Ni as well as the SO_x emissions from FCC units, the industry requires compositions that are efficient for the passivation of V and/or Ni which is present in hydrocarbon feedstocks.

15 In addition, V and/or Ni/SO_x control agents which are used in the form of separate particulate additives must have hardness and attrition properties that enable the additive to remain in a circulating FCC catalyst inventory.

It is, therefore, an object of the present invention to provide novel SO_x gettering agent/metals passivation compositions.

20 It is another object to provide metal control additives for use in FCC processes that are also efficient for SO_x pick-up and release as well as the passivation of V and/or Ni.

It is a further object to provide magnesia-lanthana-alumina containing metals/SO_x control additives that are resistant to attrition and capable of maintaining sufficiently high surface area when used in the highly abrasive and hydrothermal conditions encountered in a commercial FCC process.

25 It is yet another object to provide efficient/economical methods for preparing metals/SO_x control additives on a commercial scale.

These and still further objects will become readily apparent to one skilled-in-the-art from the following detailed description, specific examples, and drawing wherein figures 1 and 2 are block diagrams which illustrate preferred methods of preparing the novel compositions of the present invention.

30 Broadly, my invention contemplates a novel non-spinel, ternary oxide base having the formula (expressed in weight percent calculated as the oxides):

30 to 50 MgO/5 to 30 La₂O₃/30 to 50 Al₂O₃ wherein the MgO component is present as a microcrystalline phase which is particularly effective for passivating V and/or Ni as well as controlling SO_x emissions during the catalytic cracking of hydrocarbons.

35 More specifically, my invention comprises a novel MgO/La₂O₃/Al₂O₃ ternary oxide base in combination with zeolite containing catalytic cracking compositions which are used to process hydrocarbon feedstocks that contain Ni/V and/or sulfur.

The preferred additive compositions are further characterized by: A fresh surface area of 100 to 300 m²/g following 2-hour air calcination at 538 °C, and preferably 130 to 260 m²/g as determined by the B.E.T.

40 method using nitrogen; a surface area of 100 to 200 m²/g upon 48-hour steaming with 20% steam/80% air; a pore volume of 0.4 to 1.0 cc/g as determined by water; a nitrogen pore volume of at least about 0.3 cc/g, preferably 0.4 to 0.6 cc/g from nitrogen porosimetry covering up to 600 Å pore diameter at 0.967 relative pressure; an attrition resistance of 0 to 45 Davison Index (DI) as determined by the method disclosed in U.S. 3,650,988 and 4,247,420 for fresh material after 2-hour air calcination at 538 °C; a microcrystalline MgO

45 component before and after steaming as determined by X-ray diffraction; when used as an SO_x control additive, the composition preferably includes a total promoter metal content of 1 to 15 weight percent as oxides, and preferably 2 to 10% by weight ceria and/or vanadia; a sodium content of less than about 1% by weight Na₂O, and preferably less than 0.5% by weight Na₂O; and a bimodal distribution of mesopores in the 40-200 Å and 200-2000 Å regions. The median (pore volume basis) pore diameter from nitrogen 50 porosimetry ranges from approximately 50 Å to 100 Å, depending on the final calcination condition, e.g., simple air calcination at 538 °C or air calcination at 704 °C with varying levels of steam.

Referring to Figure 1, it is seen that the composition may be prepared by a multi-step process described as follows:

(1) A solution containing a lanthanum salt such as lanthanum nitrate is reacted with a solution of sodium 55 aluminate under conditions wherein a separate stream of lanthanum nitrate is combined with a stream of sodium aluminate solution over a period of 20 to 60 minutes in a stirred reaction vessel to form a lanthanum-aluminum hydrous oxide coprecipitate.

(2) The coprecipitated lanthanum-aluminum hydrous oxide slurry mixture of step (1) is aged at a pH of 9.3 to 9.7 for a period of 0.1 to 2 hours at a temperature of 20 to 65 °C.

(3) The aged slurry of step (2) is then reacted with an aqueous solution of magnesium nitrate and a solution of sodium hydroxide which are added as separate streams over a period of 20 to 60 minutes to a stirred reaction vessel at a pH of about 9.5 and at a temperature of 20 to 65 °C to obtain a ternary magnesium/lanthanum/aluminum hydrous oxide precipitate.

(4) The ternary oxide precipitate of step (3) is separated by filtration, washed with water to remove extraneous salts, preferably spray dried, and calcined at a temperature of 450 to 732 °C to obtain a ternary oxide base composition that is free of $MgAl_2O_4$ spinel and having a surface area of 130 to 260 m²/g.

(5) The ternary oxide base obtained in step (4), when used as an SO_x additive, is preferably impregnated with solutions of cerium and/or vanadium and optionally titanium to impart a ceria content of about 5 to 15 weight percent and a vanadia content of about 1 to 10 weight percent and optionally a titania content of 0 to 10 weight percent.

(6) The impregnated base of step (5) is then dried and calcined at a temperature of 450 to 700 °C.

Alternative methods for preparing the novel compositions are outlined in Figure 2 wherein: the magnesium/lanthanum/rare earth nitrate, sodium hydroxide, sodium aluminate solutions described above are combined in a mixer (typically a four-port mix-pump) to form a Mg-La/RE-Al ternary hydrous oxide coprecipitate which is aged for about 10 to 60 minutes and then further processed into particulate SO_x control additives as shown in alternative processing methods (A) and (B).

The preferred compositions of the present invention are prepared in the form of microspheres which have a particle size range of 20 to 200 microns and a Davison attrition index (DI) of 0 to 45, preferably 0 to 15, and are suitable for use as SO_x control additive in FCC processes.

The metals control additive composition may be combined with conventional commercially available FCC catalyst zeolite-containing FCC catalysts which typically contain 10 to 60 weight percent zeolite such as Type Y, ultrastable Y, ZSM-5 and/or Beta zeolite dispersed in an inorganic oxide matrix, such as the Octacat®, XP®, Super-D®, and DA® grades produced and sold by the Davison Chemical Division of W. R. Grace & Co.-Conn.

It is contemplated that the metals control SO_x control additive compositions may also be incorporated in FCC catalyst particles during manufacture in a catalyst preparation procedure such as disclosed in U.S. 3,957,689, U.S. 4,499,197, U.S. 4,542,118 and U.S. 4,458,623 and Canadian 967,136.

The metals control additive compositions (unpromoted) are typically added to a FCC catalyst in amounts ranging from 0.2 to 15 weight percent and more preferably 0.5 to 5 weight percent. In addition, the catalyst composition may include about 1 to 15 weight percent of the ceria/vanadia promoted compositions for control of SO_x emissions. The promoted/unpromoted compositions may be pre-blended prior to adding to a FCC unit. In one preferred embodiment, the FCC catalyst will also contain a noble metal combustion/oxidation catalyst such as Pt and/or Pd in amounts of 0.1 to 10 ppm. The FCC catalyst/SO_x control composition mixture is reacted with hydrocarbon gas-oil and residual feedstocks that contain as much as 2.5 weight percent sulfur (S), 0.005 weight percent Ni and/or 0.005 weight percent V, at temperatures of 520 to 1100 °C (cracking reaction) and 700 to 750 °C (regeneration). In typical commercial FCC operations it is anticipated that the FCC catalyst may accommodate up to about one weight percent Ni and/or V and still contain an acceptable level of activity and/or selectivity.

Cracking activity is determined by the so-called microactivity test (MAT) method according to ASTM #D 3907-8.

The Davison Index (DI) is determined as follows:

A sample of catalyst is analyzed to determine the weight of particles in the 0 to 20 and 20+ micron size ranges. The sample is then subjected to a 1 hour test in a fluid catalyst attrition apparatus using a hardened steel jet cup having a precision bored orifice. An air flow of 21 liters a minute is used. The Davison Index is calculated as follows:

50

$$\text{Davison Index} = \frac{\text{wt. \% 0-20 micron material formed during test}}{\text{wt. original 20 + micron fraction}}$$

55

Having described the basic aspects of my invention, the following examples are included to illustrate specific embodiments.

Example 1

A coprecipitation run was carried out by feeding one acidic stream and one basic stream simultaneously into a high speed mix-pump reactor with multiports, allowing the viscous product stream to fall into 5 4000 g of heel water in a kettle maintained at 38-40 °C with good agitation. The acidic feedstream contained 654.4 g of MgO and 413.3 g of La-rich rare earth oxide, all in the form of nitrate in a total volume of 9840 ml. The basic feedstream had a sodium aluminate solution bearing 654.4 g of Al₂O₃ along with 320 g of 50 weight percent sodium hydroxide solution in a total volume of 9840 ml. While these two streams were fed at an equal rate of 400 ml/minute, the feed rate of stream No. 3 with 16 weight percent sodium hydroxide 10 solution was adjusted so as to control pH of the slurry in the kettle at 9.4 - 9.5. After aging the slurry under this condition for 15 minutes and confirming pH was at 9.5 at the end of aging, the slurry was immediately vacuum filtered. The filtercake was then homogenized using a high-shear mixer, Drais milled once, rehomogenized, and was spray dried.

A 400 g portion of the above resulting microspheres was slurried once in 1000 g of tap water at room

15 temperature for 3 minutes, and then was washed once with another 1000 g of room-temperature tap water, and filtered. After overnight drying in a 115 °C oven, the material was air calcined at 704 °C for 2 hours. Properties of the resulting material, hereafter to be referred to as 1A, are as follows: Chemical composition (weight percent): 36.8% MgO, 20.8% La₂O₃, 0.1% CeO₂, 23.4% total rare earth oxide, 0.2% Na₂O, and 20 39.1% Al₂O₃. The results from X-ray powder diffraction scan showed that this material was virtually MgAl₂O₄ spinel-free before and after 5-hour exposure to flowing (1.5 liters/minute) air containing 20 volume % steam at 788 °C. Average particle size: 99 microns, attrition resistance: 17 DI (Davison Index), BET (N₂) surface area: 181 m²/g.

A set of four 60-gram samples was prepared by physically blending an ORION® family of Davison FCC catalyst with 0, 5, 10, and 15 weight percent (on a dry basis) of 1A. Each sample was then treated 25 according to the following protocol: Heated to 204 °C and allowed one-hour soak at this temperature in a muffle furnace; Raised at a rate of approximately 4 °C/minute to 677 °C and then allowed to soak at this temperature for 3 hours; Cooled to room temperature; Impregnated with vanadium naphthenate in pentane to completely and uniformly cover all particles with vanadium; Allowed pentane to evaporate away in a muffle furnace at room temperature; Heated to 204 °C and held for one hour; Charged into an Inconel fluid-30 bed reactor; steamed for 5 hours in this fluidized bed at 788 °C, with 80 vol.% steam (6.8 g H₂O/hour) and 20% vol.% air. Each sample was then examined for chemical and physical properties, especially the zeolite surface area. The results are presented in Table I. The data reveal unequivocally that the material 1A is highly effective in protecting zeolites in the FCC catalyst from vanadium attack. With only 5 weight percent of 1A in the blend, the zeolites in this blend retained approximately 93% more zeolite area than without 1A. 35 With 10 weight percent of 1A, there is a 122% increase in zeolite area as a result of preferential vanadium capture by the material of this invention, 1A.

Example 2

40 Another additive having a composition slightly different from 1A of Example 1 was prepared in exactly the same manner as in Example 1, except for the feedstream composition. The acidic feedstream consisted of 9840 ml of solution containing 671.6 g of MgO, 275.5 g of La-rich rare earth oxide, and 123.1 g of CeO₂, all in the form of nitrate. The basic feedstream contained 671.6 g of Al₂O₃ in the form of sodium aluminate solution along with 320 g of 50 weight percent sodium hydroxide solution in a total volume of 9840 ml.

45 The material obtained from spray drying, slurring, washing, drying, and 2 hour air calcination at 704 °C, hereafter to be referred to as 2A, had the following properties: Chemical composition (weight percent): 38.0% MgO, 13.8% La₂O₃, 5.7% CeO₂, 21.1% total rare earth oxide, 0.4% Na₂O, 0.3% SO₄, and 39.8% Al₂O₃. This material, 2A, also showed virtually no MgAl₂O₄ spinel before and after 5-hour steaming (80% steam/20% air) described in Example 1.

50 In exactly the same manner as in Example 1, another set of four 60-gram samples, ORION/2A blend, was prepared, and was treated with the same vanadium impregnation and steaming as described in Example 1. The results on this set of blends are presented in Table II. The data essentially confirm what has already been observed in Example 1.

Example 3

A 71.82 g (70.00 g on a dry basis) portion of 2A of Example 2 was sprayed with fine mist of ammoniacal vanadium tartrate solution bearing 1.80 g of V₂O₅ to incipient wetness using an atomizer and a

rotary mixer. After allowing the impregnated material to stand at room temperature for approximately 30 minutes, the material was oven dried overnight at 115 °C, and then was air calcined at 538 °C for one hour. The resulting material, hereafter to be referred to as 3A, was virtually MgAl₂O₄ spinel-free according to X-ray powder diffraction scan before and after 48-hour exposure to flowing air (1.5 liters/minute) containing 20 vol.% steam at 702 °C. The properties of this material are as follows: Chemical composition (weight percent): 35.9% MgO, 13.5% La₂O₃, 5.6% CeO₂, 20.8% total rare earth oxide, 0.4% Na₂O, 2.7% V₂O₅, and 39.4% Al₂O₃. Average particle size: 54 microns, Attrition resistance: 8 DI. BET (N₂) surface areas before and after 48-hour steaming (20% steam/80% air) were 181 and 124 m²/g, respectively.

The above resulting material, 3A, was evaluated on the bench as a potential SOx additive, i.e., SOx transfer catalyst, capturing SO₃ in the oxidizing environment of the regenerator and releasing sulfur in the form of H₂S in the reducing environment of the riser. Since the performance of SOx additive can be assessed largely by the capacity of SO₃ capture and the release capability in the form of H₂S, the following two tests were carried out for this sample:

(1) Capacity for SO₃ capture: A blend was prepared from 9.950 g of steamed (6 hours in a fluidized bed at 760 °C and 5 psig) OCTACAT® (another Davison FCC catalyst) and 0.050 g of fresh 3A, all on a dry basis. It was charged into an Inconel reactor having an I.D. of 1.04 cm, and was subjected to two-stage treatments: First, a 30-minute reduction in flowing (1.5 liters total/min.) N₂ containing 2 vol.% H₂, and next, a 30-minute oxidation in flowing (1.5 liters total/min. N₂ containing 4 vol.% O₂ and 0.0900 vol.% SO₂ at 732 °C. After each treatment, the sample was discharged, homogenized, and the sulfate level was determined on a one-gram portion removed from the sample. The weight percent SO₄ found in this sample as a result of the oxidation treatment was 0.46%. This was taken as a measure of the capacity for SO₃ capture. The capacity found for this sample represents approximately 85% of the theoretical maximum - the maximum weight percent SO₄ that can be accumulated in this sample is approximately 0.54% when all metals but aluminum form stoichiometric sulfates at 732 °C. The material of this invention, 3A, thus has a quite high capacity for SO₃ storage.

(2) Release capability: A 0.40 g sample of fresh 3A was placed in a down-flow Vycor glass reactor, and was exposed to flowing N₂ containing 9.50 vol.% O₂ and 0.6000 vol% SO₂ at a total flow rate of 126 ml/minute and 732 °C for a period of 3 hours, and cooled in flowing N₂ for discharge. A 0.10 g portion of the above-treated sample was examined by temperature-programmed reduction (TPR)/mass-spectrometer in a ramp-mode at a rate of 20 °C/min., using propane at 14.2 ml/min. as a reducing agent. During the course of this TPR run, the concentration of H₂S was determined as a function of temperature by monitoring mass number 34. The TPR scan data plot, H₂S counts vs. temperature for this sample showed an onset temperature - the temperature here represents a sort of dynamic temperature rather than equilibrium or steady/isothermal temperature - of approximately 500 °C, which is well below the riser bottom temperature. Thus, 3A is expected to show a release capability.

Example 4

Three of the four steamed samples with vanadium listed in Table I for Example 1 were evaluated by microactivity test (MAT) using a fixed bed reactor described in ASTM Method No. D3907. The feedstock employed in MAT evaluation was a sour, imported heavy gas oil with properties shown in Table III. The MAT data at constant conversion summarized in Table IV clearly demonstrate what one can expect from the materials of this invention. Namely, there is activity benefit, as reflected in the substantially decreased catalyst-to-oil weight ratio (C/O) for the FCC catalyst samples blended with some of the materials of this invention. There are also selectivity benefits - especially noticeable are the drastically lowered coke and H₂ gas yields and substantially increased gasoline yield.

Example 5

An additive with a composition very slightly different from 2A was prepared in exactly the same manner as in Example 2 by making minor changes in Mg/rare earth/Al ratio for the feedstreams. The material obtained from spray drying, followed by slurring, washing, drying, and 2-hour calcination at 538 °C, hereafter to be referred to as 5A, had the following properties: Chemical composition (weight percent): 39.1% MgO, 12.0% La₂O₃, 7.4% CeO₂, 20.7% total rare earth oxide, 0.1% Na₂O, 0.3% SO₄, and 39.6% Al₂O₃. Some of the physical properties are - 0.67 g/cc average bulk density, 73 micron average particle size, 187 m²/BET (N₂) surface area, 0.485 N₂ pore volume, 66 Å median (N₂-PV) pore diameter, and 10 DI.

A set of three 60-gram samples of ORION®/5A blend was prepared, and was steamed with vanadium in exactly the same manner as in Example 1. Properties and MAT data at constant conversion for these

samples are presented in Tables V and VI, respectively. These data essentially confirm the kind of results we have already shown in Tables I and IV for the materials of this invention.

5

TABLE I

Effect of Additive 1A on FCC Catalyst

10

Blend (Wt.) Ratio 1A/FCC Cat.	0/100	5/95	10/90	15/85
----------------------------------	-------	------	-------	-------

15

Chemical Composition (wt.%) after steaming with vanadium

20

Al_2O_3	32.63	33.02	33.35	33.44
Na_2O	0.43	0.42	0.42	0.39
SO_4	0.51	1.11	1.27	1.07
MgO	0.08	2.38	3.98	6.00
RE_2O_3	1.51	2.79	3.76	5.02
Ni	0.003	0.002	0.003	0.002
V	0.522	0.568	0.550	0.560

30

Properties after steaming with vanadium

35

Unit Cell, Å	24.23	24.23	24.24	24.23
Pk. Ht.	12	19	25	24
Total S.A., m^2/g	68	114	127	129
Zeolite S.A., m^2/g	45	83	90	89
Effective	45	87	100	105
Relative	1.00	1.93	2.22	2.32

45

50

55

TABLE II

Effect of Additive 2A on FCC Catalyst

Blend (Wt.) Ratio 2A/FCC Cat.	0/100	5/95	10/90	15/85
----------------------------------	-------	------	-------	-------

Chemical Composition (wt.%) after steaming with vanadium

Al_2O_3	32.52	32.82	32.67	34.26
Na_2O	0.44	0.43	0.42	0.43
SO_4	0.49	1.08	1.07	1.01
MgO	0.08	2.30	4.18	5.77
RE_2O_3	1.51	2.60	3.57	4.53
Ni	0.002	0.003	0.003	0.003
V	0.495	0.548	0.542	0.537

Properties after steaming with vanadium

Unit Cell, Å	24.23	24.24	24.26	24.24
Pk. Ht.	19	30	34	36
Total S.A., m^2/g	81	127	143	149
Zeolite S.A., m^2/g	53	87	99	102
Effective	53	91	110	120
Relative	1.00	1.72	2.08	2.26

Table III

Properties of Sour, Imported, Heavy Gas Oil (SINGO)

5	API gravity at 16°C	:	22.5
10	Sulfur (wt.%)	:	2.6
15	Nitrogen (wt.%)	:	0.086
20	Conradson Carbon (wt.%)	:	0.25
25	Aniline Point (°C)	:	73
30	K Factor	:	11.6
35	D-1160 (°C)	:	
40	IBP	:	217
45	5	:	307
50	10	:	324
55	20	:	343
60	40	:	382
65	60	:	423
70	80	:	472
75	90	:	500
80	95	:	524

TABLE IV

5 Interpolated, Mass-Balanced MAT Yields at 55 wt.% Conversion
 Samples: 5h/788°C Steamed (80% steam/20% air at 0 psig)
 1A/ORION® Blends with 5000 ppm V

10 Test Conditions: 527°C, 30 sec. Contact Time, SINGO Feed

	Blend wt. Ratio 1A/FCC Cat.	: 0/100	5/95	10/90
15	Cat./Oil Weight Ratio	: 5.5	3.5	3.1
MAT Yields @ 55% Conversion				
20	H ₂ C ₁ + C ₂ 's	: 0.95 : 2.3	0.52 1.8	0.36 1.6
25	C ₃ = Total C ₃ 's	: 2.8 : 3.4	3.0 3.5	3.1 3.6
30	C ₄ = iso C ₄ Total C ₄ 's	: 3.8 : 1.2 : 5.5	4.0 1.6 6.1	4.1 1.8 6.4
35	C ₅ + Gasoline	: 36.1	38.6	39.4
40	LCO 640 + Bottoms Coke	: 26.6 : 18.4 : 6.7	26.4 18.6 4.4	26.0 19.0 3.5
45	GC-RON GC-MON	: 92.6 : 81.3	91.6 80.5	91.0 80.3
50	n-Paraffins iso-Paraffins Olefins Aromatics Naphthenes	: 4.5 : 24.1 : 26.5 : 36.2 : 8.5	4.7 26.7 25.5 33.8 9.4	4.5 28.5 25.3 31.9 9.9

TABLE V

5

Effect of Additive 5A on FCC Catalyst

10

Blend (Wt.) Ratio 5A/FCC Cat.	0/100	5/95	10/90
----------------------------------	-------	------	-------

15

Chemical Composition (wt.%) after steaming with vanadium

20

Al ₂ O ₃	32.28	32.86	33.26
Na ₂ O	0.43	0.42	0.39
SO ₄	0.50	1.07	1.08
MgO	0.11	2.25	4.31
RE ₂ O ₃	1.53	2.60	3.66
Ni	0.002	0.003	0.002
V	0.511	0.525	0.537

30

Properties after steaming with vanadium

35

Unit Cell, Å	24.26	24.24	24.25
Pk. Ht.	21	32	35
SA (Z/M), m ² /g	62/29	88/36	96/42
SA (Z), Effective	62	93	107
SA (Z), Relative	1.00	1.50	1.73

45

50

55

TABLE VI

5 Interpolated, Mass-Balanced MAT Yields at 60 wt.% Conversion
 Samples: 5h/788°C Steamed (80% steam/20% air at 0 psig)
 5A/FCC Catalyst Blends with 5000 ppm V

10 Test Conditions: 527°C, 30 sec. Contact Time, SINGO Feed

	Blend wt. Ratio 5A/FCC Cat.	:	0/100	5/95	10/90
15	Cat./Oil Weight Ratio	:	5.4	4.3	3.6
20	H ₂	:	0.98	0.73	0.46
	C ₁ + C ₂ 's	:	2.4	2.1	1.9
25	C ₃ =	:	3.2	3.3	3.4
	Total C ₃ 's	:	3.8	4.0	4.1
30	C ₄ =	:	4.2	4.3	4.4
	iso C ₄	:	1.5	1.8	2.1
	Total C ₄ 's	:	6.2	6.6	7.0
35	C ₅ + Gasoline	:	39.6	40.8	41.6
40	LCO	:	25.1	24.7	24.5
	640 + Bottoms	:	14.9	15.3	15.5
	Coke	:	7.1	5.8	4.8
45	GC-RON	:	92.1	91.4	90.9
	GC-MON	:	81.2	80.9	80.6
	n-Paraffins	:	4.6	4.9	4.5
	i-Paraffins	:	27.5	29.5	31.1
	Olefins	:	22.5	21.6	21.2
	Aromatics	:	37.7	36.2	34.5
	Naphthenes	:	7.7	8.3	9.0

45 Claims

1. A composition for the passivation of metals and/or control of SOx emissions in FCC process comprising:
 - 50 (a) a coprecipitated ternary oxide composition having the formula:
 30 to 50 MgO/5 to 30 La₂O₃/30 to 50 Al₂O₃ wherein the amounts of MgO, La₂O₃ and Al₂O₃ are expressed as weight percent, and the MgO is present as a microcrystalline component; and up to 15 weight percent of
 - (b) the composition of (a) combined with a catalytically active amount of promoters for SO₂ oxidation and/or H₂S release selected from the oxides of Ce, Pr, Ti, Nb, V and mixtures thereof.
2. The composition of claim 1 further characterized by the absence of a spinel phase, a surface area of 100 m²/g to 300 m²/g, and a Na₂O content of below about 1% by weight.

3. The composition of claim 2 wherein the surface area is 130 to 200 m²/g.
4. The composition of claim 2 having a surface area of 100 to 150 m²/g after heating to 704 °C for 48 hours in the presence of 20% steam/80% air.
5. The composition of claim 1, combined with an FCC catalyst.
6. The composition of claim 1 wherein said La₂O₃ is derived from a La-enriched rare earth mixture.
- 10 7. The composition of claim 5 wherein the FCC catalyst includes an oxidation catalyst selected from the group consisting of Pt, Pd and mixtures thereof.
8. The composition of claim 5 wherein the FCC catalyst comprises a zeolite selected from the group consisting of Type Y, ultrastable Y, ZSM-5, Beta and mixtures thereof dispersed in an inorganic oxide matrix.
- 15 9. A method for passivating V and Ni and/or controlling SOx emissions from an FCC catalyst regeneration process which comprises catalytically cracking metals and/or sulfur containing hydrocarbon in the presence of the composition of claim 5 or 6.
- 20 10. The method of claim 8 wherein said feedstock contains V and/or Ni and the FCC catalyst includes composition (a) of claim 1.

25

30

35

40

45

50

55

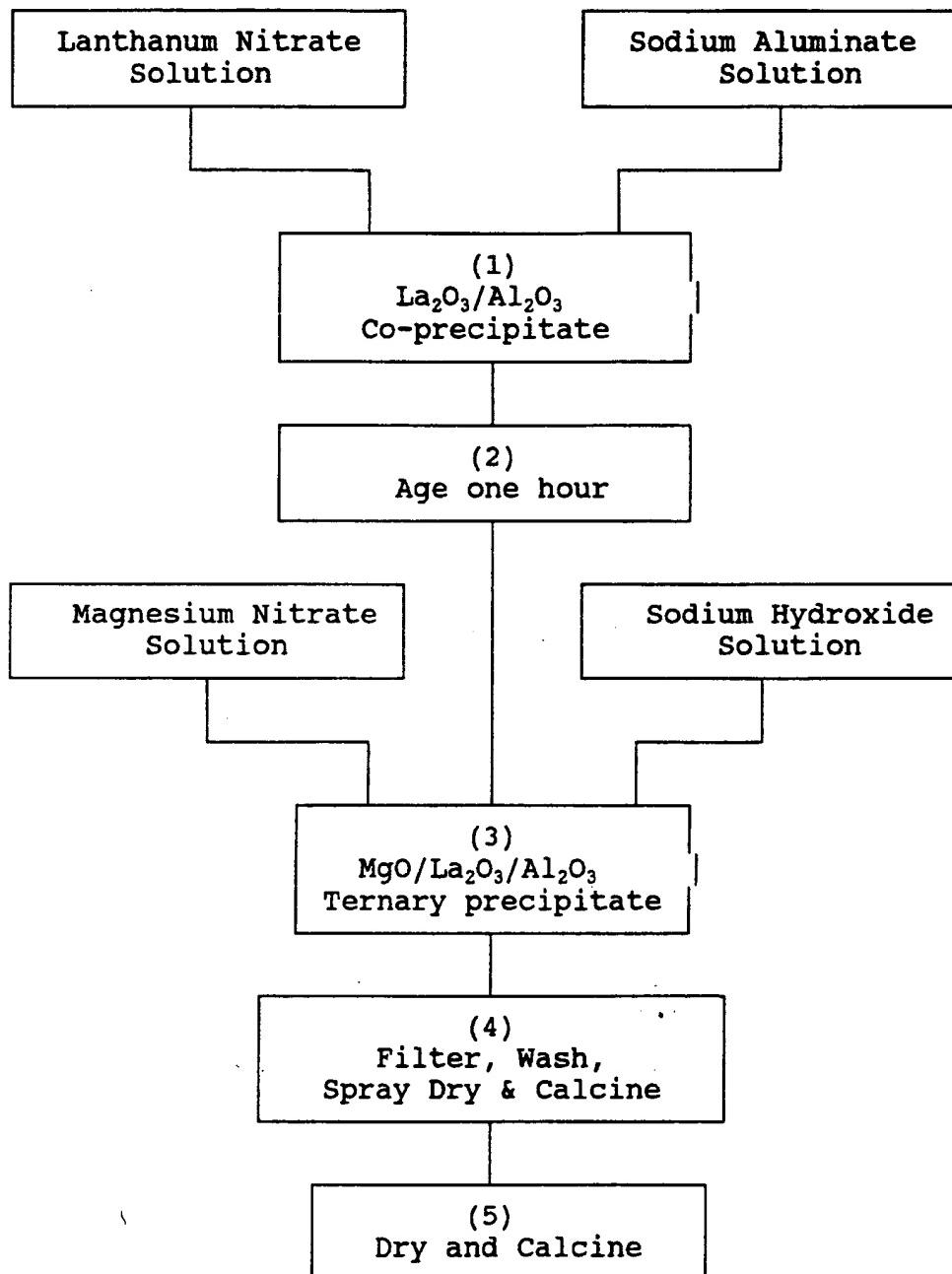
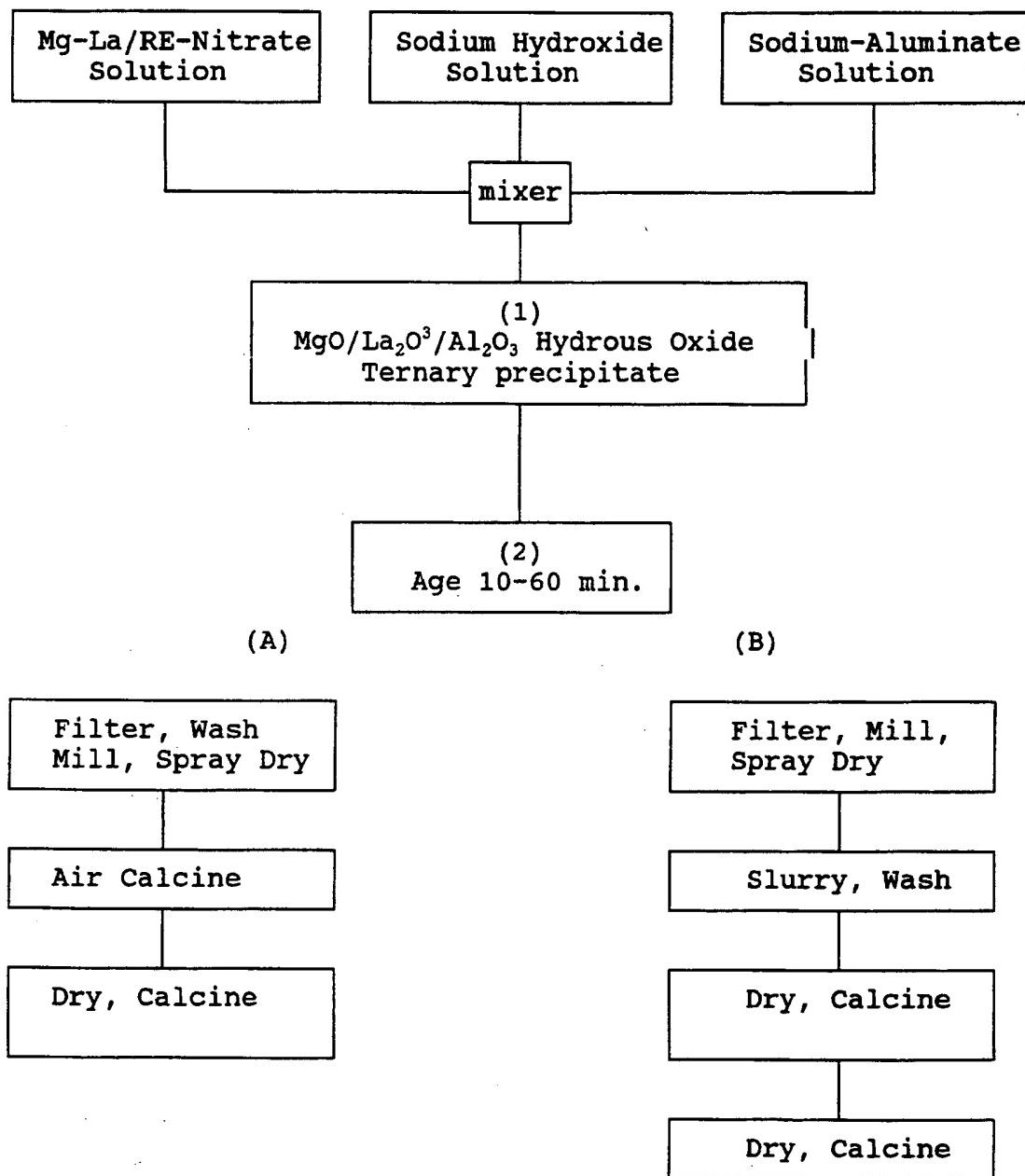
FIGURE I

FIGURE II



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 93250038.2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	<u>US - A - 4 369 130</u> (BERTOLACINI et al.) * Totality * --	1-10	C 10 G 11/18 C 10 G 11/02 B 01 J 21/00 B 01 J 29/00
A	<u>US - A - 4 423 019</u> (BERTOLACINI et al.) * Totality * --	1-10	
A	<u>US - A - 4 497 902</u> (BERTOLACINI et al.) * Totality * -----	1-10	
TECHNICAL FIELDS SEARCHED (Int. Cl.5)			
C 10 G B 01 J			
The present search report has been drawn up for all claims			
Place of search VIENNA	Date of completion of the search 10-05-1993	Examiner BECK	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record.**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)